Ligand-Driven Spin-Crossover Behavior of Fe^{II} Molecules

Do Viet Thang^{1,2,*1}, Nguyen Van Thanh^{1,*1}, Nguyen Thi Hien^{1,*1},
Nguyen Huy Sinh^{1,3} and Nguyen Anh Tuan^{1,4,5,*2}

¹Faculty of Physics, VNU University of Science, 334 Nguyen Trai, Thanh Xuan, Ha Noi, Vietnam

²Faculty of Science, Haiphong University, 171 Phan Dang Luu, Kien An, Hai Phong, Vietnam

³Hung Yen University of Technology and Education, Dan Tien, Khoai Chau, Hung Yen, Vietnam

⁴Hanoi Metropolitan University, 98 Duong Quang Ham, Cau Giay, Hanoi, Vietnam

⁵Japan Advanced Institute of Science and Technology, Nomi 923-1292, Japan

In order to explore a way to tailor thermal hysteresis behavior of spin-crossover (SCO) complexes, a series of seven Fe^{II}(LX₂) complexes with different ligand configurations has been designed or reconstructed. These Fe^{II}(LX₂) complexes differ in axial ligands X = Py, CNPY, NC₅H₄CH₃, NC₅H₄OCH₃, NC₅H₄Cl, X = NC₅H₄Br, and Him. Geometric structure, electronic structure, and magnetic properties of Fe^{II}(LX₂) complexes have been investigated using density-functional theory with full geometry optimization. Our calculated results show that the spin-state electrostatic-energy difference (ΔU) of these Fe^{II} SCO complexes can be tailored by adjusting the pK_a constant of axial ligands X. The increase of ΔU of these Fe^{II} SCO complexes from -12.18 eV to 6.64 eV results from the increase of pK_a constant of axial ligands X from 1.10 to 7.00. The role of axial ligands X in determining SCO behavior of Fe^{II} SCO complexes has been revealed. In addition, our previous study (N. A. Tuan: J. Appl. Phys. 111 (2012) 07D101) demonstrated that thermal hysteresis of spin-crossover increased with the ΔU of Fe^{II} SCO complexes. These results would give some hints into how thermal hysteresis can be tailored in Fe^{II} SCO complexes. [doi:10.2320/matertrans.M2015368]

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1. Introduction

Spin crossover (SCO) complexes is one of the most spectacular examples of molecule-based switchable materials. They can exist in two different spin states, i.e. high spin (HS) and low spin (LS) states. Switching between the HS and LS can be made by means of light irradiation, temperature, or pressure. Upon SCO, magnetic, optical, and electric properties of SCO complexes are changed.^{1,2} This leads to various applications such as sensors, molecular switches, display and memory devices.³ For some applications, high spin-crossover temperature (T_{SCO}) and wide thermal hysteresis of SCO (ΔT_{SCO}) are required, especially for memory devices. Therefore, great efforts have been paid for controlling T_{SCO} and ΔT_{SCO} .⁴ In addition, seeking factors determining T_{SCO} and ΔT_{SCO} has been extensively studied.⁵⁻⁷ In the crystal structure, spin-crossover molecules are linked by weak intermolecular interactions. In most literature, the thermal hysteresis are attributed to hydrogen bonding, π -stacking, van der Waals network. Recently, the origin of thermal hysteresis of SCO molecules results from temperature-induced electron trapping.^{8,9} Our previous study demonstrated that ΔT_{SCO} increased with the spin-state electrostatic-energy difference (ΔU) of Fe^{II} SCO complexes.¹⁰

In this paper, a series of Fe^{II}(LX₂) complexes with different ligand configurations have been designed or reconstructed. These Fe^{II} complexes have the same equatorial ligand L²⁻ = {diethyl(E,E)-2,2'-[1,2-phenylnis(iminomethylidene)]-bis[3-oxobutanoate](2-)-N,N',O³,O^{3'}} but differ in axial ligands X = CNPy (**1**), X = NC₅H₄Br (**2**), NC₅H₄Cl (**3**), Py (**4**), NC₅H₄CH₃ (**5**), NC₅H₄OCH₃ (**6**), and Him (**7**), in which molecules (**1**) and (**7**) have been synthesized.¹¹⁻¹³ Their

geometric structure, electronic structure, and magnetic properties have been examined in order to determine the role of ligands in tailoring SCO behavior of Fe^{II} complexes.

2. Computational Method

In this study, all calculations were performed by using the DMol³ code¹⁴) based on density-functional theory with the spin-unrestricted scheme. Geometric structure and electronic structure of Fe^{II} SCO molecules were computed with full geometry optimization, allowing the relaxation of all atoms in this molecule. In the optimization process, the energy, energy gradient, and atomic displacement are converged to 1×10^{-5} , 1×10^{-4} and 1×10^{-3} a.u., respectively. In the self-consistent calculation, the charge density is converged to 1×10^{-6} a.u. To obtain both the geometric structures corresponding to the LS and HS states of Fe^{II} molecules, both the LS and HS configurations of the Fe^{II} ion are probed. For better accuracy, the double numerical basis sets plus polarization (DNP) functional was used. The real-space global cutoff radius was set to be 0.7 nm for all atoms. The hexadecapolar expansion scheme was adopted for resolving the charge density and Coulombic potential. The generalized gradient approximation (GGA) PBE functional was used¹⁵) to describe the exchange correlation energy in Fe^{II} SCO molecules. The effective core potential Dolg-Wedig-Stoll-Preuss^{16,17}) was applied to describe the interaction between the core and valence electrons. The charge and magnetic moment of atoms in Fe^{II} SCO molecules were obtained by using the Mulliken population analysis.^{18,19}

3. Results and Discussions

The schematic geometric structure of Fe^{II}(LX₂) molecules (**1**)–(**7**) is depicted in Fig. 1. As shown in Fig. 1, each molecule consists of one Fe atom located in the distorted

*1Graduate Student, VNU University of Science

*2Corresponding author, E-mail: tuanna2910@gmail.com, natuan@daihocthuo.edu.vn

Fig. 1 The schematic geometric structures of molecules (1)–(7), and the ligand configuration of Fe^{II} atom. H atoms are removed for clarity. Color code: Fe: violet, O: red, N: blue, C: grey.

Table 1 Fe–N/O bond lengths (nm) of (1) and (7) in the LS and HS states. The experimental data are shown in bold.^{11–13)}

	(1)		(7)	
	LS	HS	LS	HS
Fe–O1	0.1947	0.1946	0.1992	0.1999
Fe–N1	0.1895	0.1906	0.2028	0.2093
Fe–N2	0.1899	0.1907	0.2037	0.2095
Fe–O2	0.1942	0.1946	0.1970	0.1999
Fe–N3	0.1979	0.1957	0.2238	0.2384
Fe–N4	0.1986	0.1987	0.2177	0.2185

octahedron, in which the tetradentate N₂O₂-coordinating ligand (L) stands in the equatorial plane, and two equivalent terminal neutral N-coordinating ligands (X) complete the coordination sphere. These Fe^{II}(LX₂) molecules can exist in two geometric structures corresponding to the low-spin (LS) state with the total spin $S = 0$ and the high-spin (HS) state with $S = 2$. The computed geometric structures of (1) and (7) are slightly different in experimental data reported in references,^{11–13)} as shown in Table 1. Here, it is noted that these calculations have been carried out for isolated molecules in vacuum. This approximation neglects the interactions between neighbouring molecules. Calculations which do not regard these interactions can therefore be different from the experiment. Nevertheless, such calculations for isolated molecules in vacuum may reveal information about the molecular contribution to substituent-induced shifts of SCO characteristics. This information can hardly be gained experimentally since any experiment with a solid sample will only reflect the combined influence of intra- and inter-molecular interactions.

The atomic arrangement in the LS and HS states that each of the molecules (1)–(7) is the same, however, inter-atomic distances are different, as shown in Table 1. The Fe–ligand bond lengths increase upon SCO from the LS state to the HS state. This result can be explained in terms of ligand field theory. In these Fe^{II} molecules, the Fe^{II} ion is located in nearly octahedron forming by four anionic nitrogen ions and two anionic oxygen ions, as shown in Fig. 1. In terms of octahedral ligand field, the LS state of the Fe^{II} is (t_{2g}^6, e_g^0) characterized by three fully occupied t_{2g} orbitals ($d_{xy}^2, d_{xz}^2,$

Table 2 The charge of Fe and surrounding atoms in the LS state (n_{LS}) and the HS state (n_{HS}) of molecules (1), (6) and (7).

	(1)			(6)			(7)		
	n_{LS}	n_{HS}	n_{HS}/n_{LS}	n_{LS}	n_{HS}	n_{HS}/n_{LS}	n_{LS}	n_{HS}	n_{HS}/n_{LS}
Fe	0.474	0.947	1.998	0.464	0.941	2.028	0.466	0.954	2.047
O1	−0.468	−0.541	1.156	−0.465	−0.536	1.153	−0.432	−0.512	1.185
O2	−0.470	−0.544	1.157	−0.465	−0.537	1.155	−0.434	−0.523	1.205
N1	−0.423	−0.484	1.144	−0.414	−0.477	1.152	−0.407	−0.477	1.172
N2	−0.423	−0.483	1.142	−0.414	−0.479	1.157	−0.405	−0.470	1.160
N3	−0.364	−0.440	1.209	−0.388	−0.439	1.131	−0.360	−0.421	1.169
N4	−0.376	−0.389	1.035	−0.379	−0.424	1.119	−0.359	−0.422	1.175

d_{yz}^2) and by two empty e_g orbitals ($d_{x^2-y^2}^0, d_{z^2}^0$). Upon SCO from the LS state to the HS state, two electrons are transferred from t_{2g} orbitals to e_g orbitals. The electronic configuration of the HS state is (t_{2g}^4, e_g^2). It is easy to notice that e_g orbitals are single occupied in the HS state, while they are empty in the LS state. As we know, the electron density in e_g orbitals is directed toward six anionic ions surrounding the Fe^{II} ion, while the electron density in t_{2g} orbitals is distributed along the bisector of the ligand–Fe–ligand angles. Therefore, coulomb repulsion to anionic ions from e_g electrons is stronger than that from t_{2g} electrons. Consequently, the Fe–N/O bond lengths of the HS state are longer than those of the LS state, as shown in Table 1. In more details, the Fe–O1 and Fe–O2 bond lengths only increase slightly from about 1.5% to 3.5%, while the Fe–N bond lengths increase significantly by about 10%. These demonstrate that the Fe–O bonds are stronger than the Fe–N bonds. Therefore, the Fe–O bonds play an important role in the stability of these Fe^{II} molecules, while the Fe–N bonds play a crucial role in SCO behavior of these Fe^{II} molecules. Hence, by variation in the X ligand, the Fe–N3 and Fe–N4 bonds as well as SCO behavior of Fe^{II}(LX₂) molecules can be tailored.

Our calculated results show that the transition from the LS state to the HS state is not only accompanied with the increase of Fe–ligand bond lengths, but also the interatomic charge (electron) transfer from the Fe atom to ligands. Upon SCO from the LS to HS, about 0.5e is transferred from the Fe atom to ligands, as illustrated in Table 2. These results can be explained in terms of the delocalization of 3d electrons of metals transition, so 3d electrons are less delocalized in the LS state, being more delocalized in the HS state.²⁰⁾ This process makes change in the electrostatic energy (U) as well as the total electronic energy (E) of SCO molecules, as shown in Table 3. Moreover, in our previous study,⁷⁾ our results demonstrated that ΔT_{SCO} increased with the spin-state electrostatic-energy difference ($\Delta U = U_{HS} - U_{LS}$) of Fe^{II} SCO complexes, and T_{SCO} increased with the total electronic energy difference ($\Delta E = E_{HS} - E_{LS}$). It poses a question which parameters determine ΔE and ΔU of Fe^{II} SCO complexes. It is noted that, molecules (1)–(7) are only different in axial ligands X = CNPy (1), X = NC₅H₄Br (2), NC₅H₄Cl (3), Py (4), NC₅H₄CH₃ (5), NC₅H₄OCH₃ (6), and Him (7). In order to find out the key parameters in determining ΔU of molecules (1)–(7), we consider several electronic parameters of these ligands, one of which is the

Table 3 The energy differences [eV] between the LS and HS states of molecules (1)–(7), including: the kinetic energy difference (ΔK), the electrostatic energy difference (ΔU), the exchange-correlation difference (ΔE_{xc}), and the total electronic energy difference (ΔE).

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
pK_a	1.10	3.03	3.83	5.25	6.03	6.62	7.00
ΔK	12.721	7.724	5.443	4.598	3.030	−0.283	−6.406
ΔU	−12.181	−7.284	−5.038	−4.180	−2.641	0.627	6.640
ΔE_{xc}	−0.001	0.003	0.037	0.029	0.045	0.060	0.103
ΔE	0.539	0.443	0.442	0.447	0.434	0.404	0.338

pK_a constant, the logarithmic measure of the acid dissociation constant of the axial ligands X. The pK_a constant relates to the electronic structure of X ligands, therefore, determines the interaction between electron clouds of the Fe ion and X ligands through the aromatic resonance ring of X ligands. Indeed, we find out that there is strong correlation between the pK_a constant of the axial ligands X and the value of ΔE and ΔU of molecules (1)–(7), as shown in Table 3. The ΔU rapidly increases from −12.721 eV with $pK_a = 1.1$ for (1) to 6.640 eV with $pK_a = 7$ for (7). Besides, ΔE decreases from 0.539 eV for (1) to 0.338 eV for (7) with the increase of pK_a of the axial ligands X. Molecule (1) has stepwise spin transition with no thermal hysteresis,¹¹ while molecule (7) has abrupt spin transition with $T_1 = 314$ K and $T_2 = 244$ K resulting in wide thermal hysteresis $\Delta T_{SCO} = 70$ K.¹² Moreover, our previous study showed that ΔT_{SCO} increased with ΔU of Fe^{II} SCO complexes.¹⁰ These results allow us to predict that designed $Fe^{II}(LX_2)$ molecules (2)–(6) with ΔE in the range of [0.404, 0.443] eV should be SCO complexes with thermal hysteresis ΔT_{SCO} in the range from 0 to 70 K. Our results clearly demonstrate that ΔE and ΔU of $Fe^{II}(LX_2)$ molecules can be tailored by variation in the axial ligand X, and the pK_a constant of X is a key parameter for determining ΔE and ΔU , and thus ΔT_{SCO} of $Fe^{II}(LX_2)$ complexes.

4. Conclusion

In order to explore a way to tailor SCO behavior of transition metal complexes, seven $Fe^{II}(LX_2)$ molecules (with L = constant and X = various) have been investigated based on density-functional theory. Our results point out that Fe–O bonds play an important role in the stability of $Fe^{II}(LX_2)$ molecules, while Fe–N bonds play a crucial role in SCO behavior of $Fe^{II}(LX_2)$ molecules. By variation in the X

ligand, the Fe–N3 and Fe–N4 bonds as well as SCO behavior of $Fe^{II}(LX_2)$ molecules can be tailored. Our results demonstrate that there is strong correlation between the pK_a constant of the axial ligands X and the value of the spin-state energy difference (ΔE) and the electrostatic energy difference (ΔU) of $Fe^{II}(LX_2)$ molecules. The ΔU increases with the pK_a constant of axial ligands X, while the ΔE decreases with the increase of the pK_a constant. These results would give some hints for tailoring and designing new SCO complexes with expected ΔU as well as thermal hysteresis ΔT_{SCO} .

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